

Conjugation

The Interconnection of Two Positive Charges by Conjugation and Cross-Conjugation in Bis-Quinolinium Ethynyls

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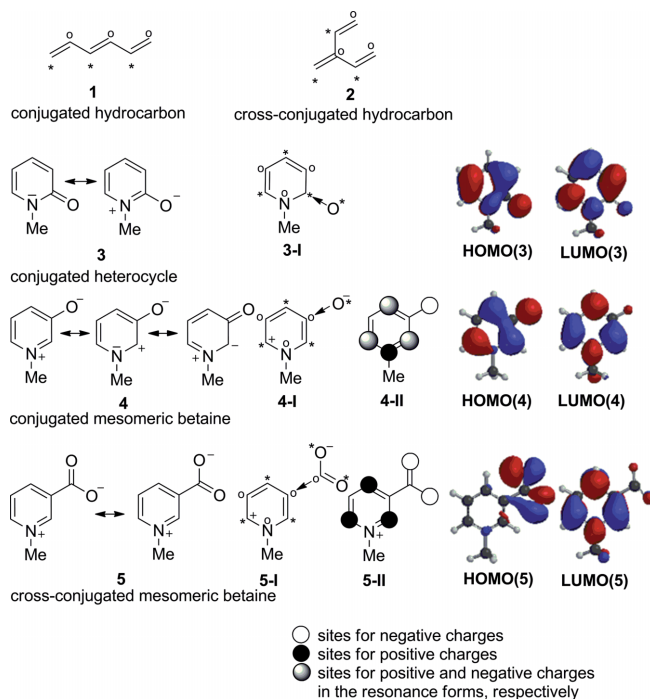
Abstract: 1,4-Diethynylbenzene was used as conjugated all-carbon and rigid spacer between the 2-, 3- and 4-positions of two 1-methylquinolinium rings. Thus, for a systematic study, a series of dicationic salts with 2,2-, 3,3-, 4,4-, 3,2-, and 3,4-interconnections of the two positive charges was prepared, in which all even-numbered substitution patterns are conjugated, and all odd-numbered substitution patterns are cross-conjugated. As a consequence, conjugated/conjugated, cross-conjugated/cross-

conjugated, and conjugated/cross-conjugated dications have been prepared. The different combinations result in considerably different charge distributions of the positive charges within the π -electron systems according to the rules of resonance which translate into different DFT-calculated frontier orbital profiles and spectroscopic properties such as ^{13}C NMR chemical shifts, IR and Raman absorptions, and the measured as well as calculated UV/Vis spectra.

Introduction

The type of conjugation of π -electronic systems greatly governs their chemical and physical characteristics. In hydrocarbon chemistry, the term “cross-conjugation”^[1] has been used to characterize any compound possessing branched conjugated systems^[2,3] with a more disjointed electronic communication in comparison to linear conjugated systems in which the delocalization is thought to be more significant.^[4] In the case of polyenes and related hydrocarbons, for example, cross-conjugated dendralenes display remarkable inhibitions of the delocalization compared to linear polyenes so that they can be considered as sets of isolated butadiene units.^[2] Considerable effort is currently being directed toward studying the differences of linear conjugation in comparison to cross-conjugation of organic molecules from the perspective of computational chemistry,^[5] materials chemistry of electrochromic molecules,^[6] heteroelement chemistry for which phenylene-bridged 1,2,3-trisilacyclopentadienes can be given as an example here,^[7] polymer chemistry,^[8] and even mathematics.^[9] Scheme 1 shows 1,3,5-hexatriene **1** as an example of Kekulé even alternant hydrocarbons, which generally have classical polyene structures,^[10] as well as its cross-conjugated isomer 3-methylenepenta-1,4-diene **2**. In alternant hydrocarbons atoms of like parity are not directly bonded, i.e. all bonds are those of starred (*) to unstarred (°)

atoms. Heterocyclic molecules which contain classical Kekulé fragments in addition to one or more 2π heteroatoms such as nitrogen, for which pyridone **3** is an example, can be represented by fully covalent neutral structures with alternating double bonds and pairs of electrons located on each heteroatom, although zwitterionic resonance forms can be drawn. The oxygen of pyridone **3** is attached to a starred position of the pyridine ring (**3-I**).



Scheme 1. Some characteristics of conjugation and cross-conjugation.

The distinction between different types of conjugation has gained great importance for the classification and deeper un-

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Understanding of the chemical and physical properties of heterocyclic mesomeric betaines. For example, installing the oxygen to the 3-position of a pyridinium ring results in the construction of a conjugated heterocyclic mesomeric betaine (CMB).^[11,12] These can exclusively be represented by dipolar canonical forms in which the positive and the negative charges are delocalized within the common π -electron system. Betaine **3** is isoconjugated with an odd alternant hydrocarbon,^[11] in which the substituent at C3 is a starred position (**4-I**). Common sites for positive and negative charges exist in the resonance forms as shown by **4-II**. By contrast, in cross-conjugated heterocyclic mesomeric betaines such as **5**, the charges are exclusively delocalized in separated parts of the π -electron system. The anionic partial structure – the carboxylate – is joined to the cationic partial structure through its unstarred position (**5-I**). No common sites for positive and negative charges exist in the resonance forms (**5-II**). The physical and chemical consequences are significant.^[11,12] Thus, the permanent dipole moments differ considerably.^[13] Conjugated mesomeric betaines mainly undergo 1,3-dipolar cycloadditions, whereas the cross-conjugated mesomeric betaines react predominantly as 1,4-dipoles.^[11] The differences are also well reflected in the frontier orbital profiles. The highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of the conjugated systems **3** and **4** are very similar. By contrast, the HOMO of the cross-conjugated mesomeric betaine **5** is almost exclusively located in the carboxylate fragment, whereas the LUMO is essentially located in the pyridinium ring. Recently, five distinct types of conjugation have been identified in heterocyclic mesomeric betaines by a matrix-connectivity analysis,^[14] so that research in the field of conjugation gets an additional impetus.

In continuation of our projects dealing with oligocationic heteroaromatics^[15] as well as mesomeric betaines^[16] and the translation of their distinct types of conjugation into chemistry such as N-heterocyclic carbene formations,^[17] we became inter-

ested in interconnecting two positive charges by conjugation and cross-conjugation and to compare the properties of the resulting systems. Series of combinations are possible by joining unsaturated spacers between the 2-, 3-, or 4-positions of two pyridinium rings, respectively (Scheme 2). A 2-yl and 4-yl substitution results in a starred position at the terminal acetylene position of the building block C*, which can itself be joined to a starred (C2, C4) or to an unstarred position (C3) of the second pyridinium. *Vice versa*, the unstarred terminal acetylene C°, resulting from substitution at C3 of the pyridinium, can be joined to the 2-, 3-, and 4-positions of the second pyridinium ring. This results in all possible π -electronic communications by conjugation/cross-conjugation combinations between two cationic substituents and enables the study of spectroscopic consequences.

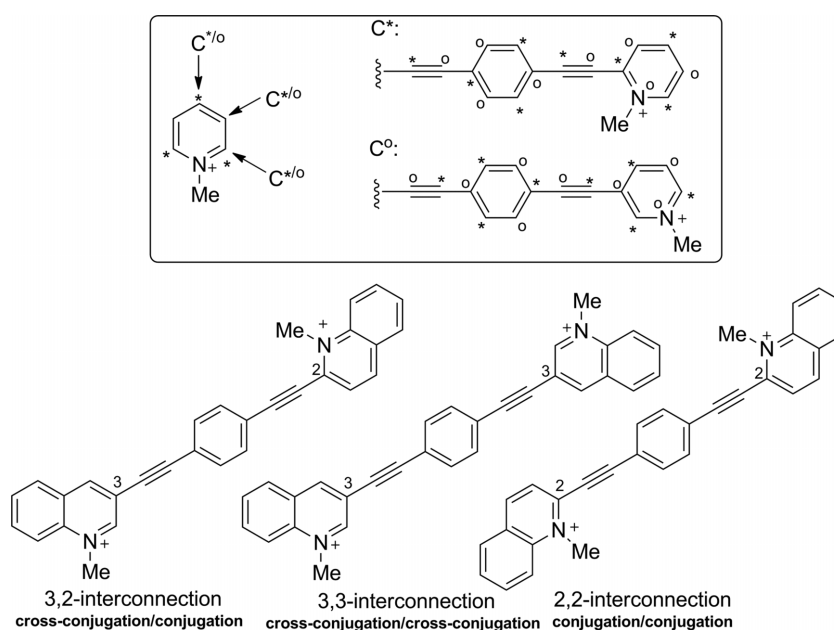
We chose the quinolinium cation as a model compound to take advantage of the additional stabilization by the benzo annelation, and 1,4-diethynylbenzene as all-carbon linker molecules to exclude the influence of configuration.

Results and Discussion

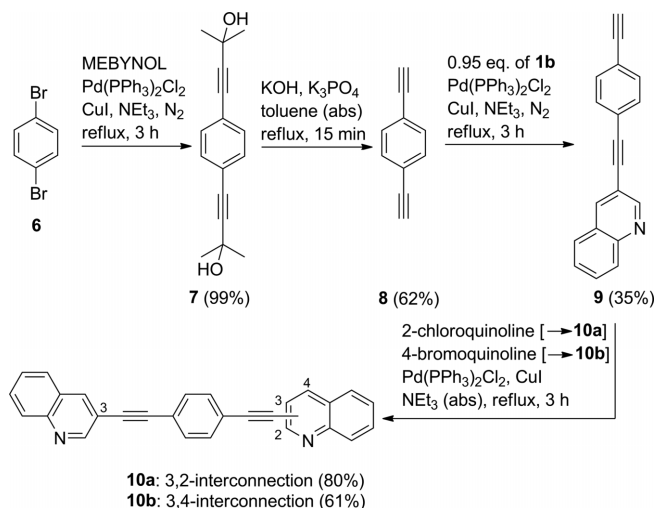
First, 1,4-diethynylbenzene **8** was synthesized in two steps from 1,4-dibromobenzene **6** and 2-methyl-butyn-2-ol (MEBYNOL) via **7** according to modified literature-known procedures^[18] (Scheme 3). The non-symmetric ethynyl quinolines **10a,b** were finally prepared in two consecutive Sonogashira reactions.^[19]

Subsequently, 1,4-diethynylbenzene **8** was treated with an excess of halogenated quinolines under Sonogashira conditions to give the symmetric ethynyl quinolines **10c–e**^[18,19] (Scheme 4).

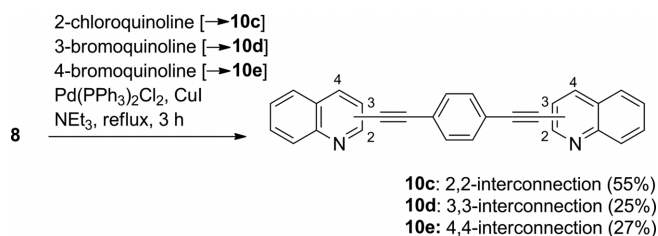
For the preparation of dicationic species, an excess (2.5 equiv.) of dimethyl sulfate was used (Scheme 5). The salts **11a–e** were formed in almost quantitative yields. Changing the



Scheme 2. Systematic design of model compounds for this study. Some examples.

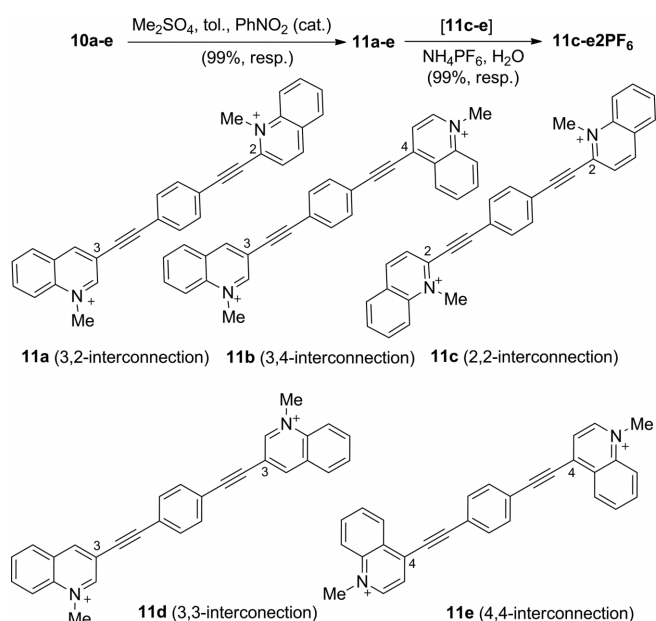


Scheme 3. Synthesis of non-symmetric diquinoline compounds connected via 1,4-di(ethynyl)benzene spacers.



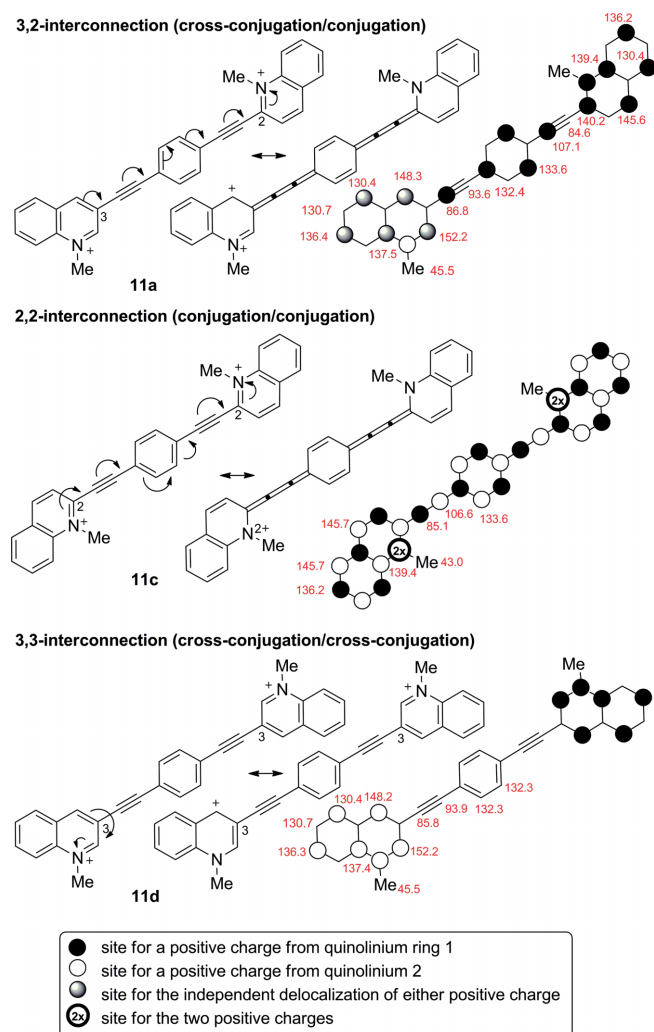
Scheme 4. Synthesis of symmetric diquinoline compounds connected via 1,4-di(ethynyl)benzene spacers.

counterions to dihexafluorophosphates then gave the salts **11c–e2PF₆** the spectroscopic properties of which do not differ considerably from those of **11c–e**.



Scheme 5. Synthesis of diquinolinium salts. The anions (2 MeSO₄[−] or 2 PF₆[−], respectively) were omitted for the sake of clarity.

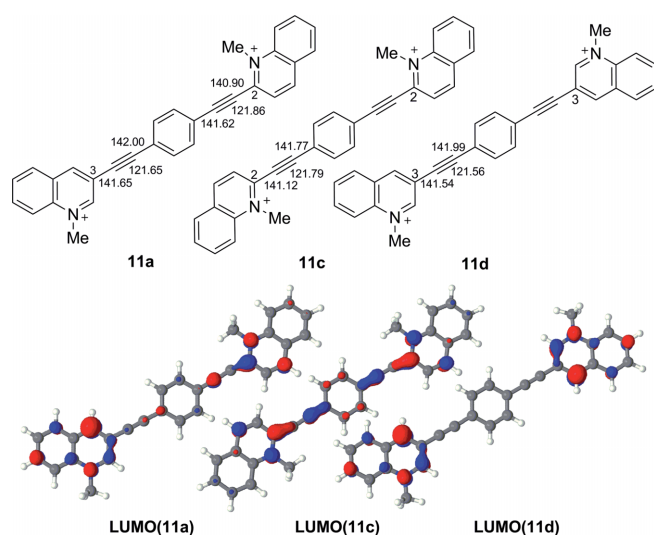
The different interconnections translate into different charge distributions according to the rules of resonance and cause characteristic spectroscopic properties. Thus, the 3,2-interconnection of dication **11a** allows for the formulation of the positive charge of the conjugated quinolinium-2-yl substituent on the nitrogen atom as well as on every second atom of the entire π -conjugated system. Bearing in mind that not all canonical forms contribute equally to the true molecule according to the rules of resonance,^[20] this formal distribution includes, however, the quinolinium-3-yl-substituent, which is by itself in cross-conjugation to the ethynyl linker. Therefore the positive charge of the quinolinium-3-yl substituent of **11a** can exclusively be formulated within the heteroaromatic. Its cross-conjugation prevents the delocalization of the positive charge into the spacer. As a consequence, five atoms can be identified as possible independent sites of either positive charge. The 2,2-interconnection of the two positive charges of **11c**, however, allows for the formulation of the charges on every atom of the π -electron system, and the nitrogen atoms are formal sites for both of them. This mesomeric structure undoubtedly is highly unfavorable,



Scheme 6. Selected mesomeric forms of **11a** (above), **11c** (middle), and **11d** (below), and charge distribution according to the rules of resonance. Selected ¹³C NMR signals.

although it is allowed according to the rules of resonance. By contrast, the 3,3-interconnection of **11d** with two quinolinium rings in cross-conjugation with respect to the spacer causes a separation of the positive charges of the quinolinium rings, respectively, according to the rules of resonance. Marked differences can be seen in the ^{13}C NMR spectra of **11a,c,d**. Obviously, triple bonds in conjugation (2-yl or 4-yl) are much more polarized than those in cross-conjugation (3-yl). As an example, the $\text{C}\equiv\text{C}$ resonance frequencies of **11c** appear at 85.1 ppm/106.6 ppm (conjugation/conjugation) and at 85.8 ppm/93.9 ppm in **11d** (cross-conjugation/cross-conjugation). As expected from the resonance forms, the quinolinium- $\text{C}\equiv\text{C}-\text{C}_6\text{H}_4$ -atom is more affected than quinolinium- $\text{C}\equiv\text{C}-\text{C}_6\text{H}_4$ -carbon atom. The 3,2-interconnection of **11a** (cross-conjugation/conjugation) shows the chemical shifts of both types of conjugation at 86.8/93.6 ppm and 84.6/107.1 ppm. The quinolinium-3-yl- $\text{C}\equiv\text{C}-\text{C}_6\text{H}_4$ -signal is shifted more downfield in agreement with its characterization as a possible site for the positive charge in the resonance forms. The selected values which are assigned to the structures in Scheme 6 show that the ^{13}C NMR signals of some positions are not influenced significantly. Very similar effects can be observed for the 3,4- and 4,4-interconnections (cf. Supporting Information).

DFT calculations (6-31G*/PBE0) of the salts **11a,c,d** show that all three isomers are planar. The methyl groups adopt a *trans* configuration as shown. Some values of calculated bond lengths are presented in Scheme 7. All triple bonds are slightly longer than in the $\text{C}\equiv\text{C}$ triple bond of acetylene (118 pm) according to the calculation, and the adjacent single bonds are shorter than literature values of $\text{C}_{\text{sp}}^2-\text{C}_{\text{sp}}$ bonds (e.g. 143 pm in vinylacetylene). These can be seen as small contributions of cumulene-type resonance structures, especially in **11a** and **11c**. The calculated HOMO/LUMO profiles of the isomers also differ characteristically. The LUMO profiles of **11a,c,d** clearly reflect the delocalization of two positive charges in conjugated systems obtained from their mesomeric structures. In all three cases, the LUMO atomic orbital coefficients of fused phenyl



Scheme 7. Selected bond lengths in pm (above) and lowest unoccupied molecular orbitals (below).

rings are smaller than the analogous coefficients in the pyridine ring. The HOMO profiles in all three cases are comparable and carry the highest atomic orbital coefficients on the $\text{C}\equiv\text{C}$ triple bonds and on the central phenyl ring (cf. Supporting Information).

The IR absorption spectra also reflect the differences between conjugation and cross-conjugation (Figure 1). Thus, the $\text{C}\equiv\text{C}$ triple bond absorption values in the corresponding IR spectra of **11d** are 2219 cm^{-1} , but 2203 cm^{-1} of **11a** and 2200 cm^{-1} of **11c**. The Raman spectra showed similar absorption values of the triple bonds at 2219 cm^{-1} (**11d**) and 2206 cm^{-1} (**11c**). Consequently, **11a** displays two absorption values at 2204 cm^{-1} and 2219 cm^{-1} (shoulder).

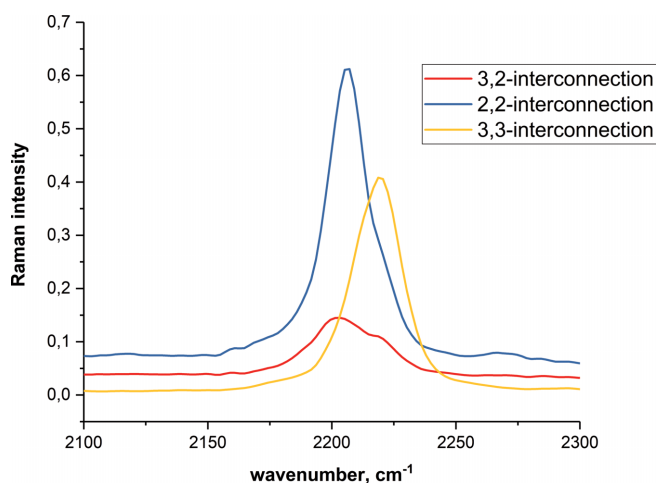


Figure 1. Raman spectra of **11a,c,d**.

The distinct types of conjugation of the π -extended dicationic salts **11a-e** are also well expressed by their UV/Vis spectra (Figure 2). Thus, the salts **11c,e** possessing conjugated 2,2-/4,4-interconnections display absorption maxima at approximately 408 nm, whereas the salt **11d** with cross-conjugated 3,3-interconnections shows a maximum at 369 nm. The salts **11a,b** possessing either type of conjugation (2,3- and 4,3-interconnections) show peaks at 394 nm in acetonitrile, respectively.

Calculations of the UV/Vis spectra for the three dicationic salts **11a,c,d** as model compounds were performed with the 6-31G* basis set and PBE0 density functional. Calculations did not include the influence of solvents, from which an impact can be expected with increasing polarity; however, changing the solvent from acetonitrile ($E_{\text{T}}(30)$ 45.6; E_{T}^{N} 0.460) to methanol ($E_{\text{T}}(30)$ 55.4; E_{T}^{N} 0.762) causes essentially no solvatochromism as can be seen from all experimental UV/Vis spectra shown in the Supporting Information. The calculated UV transitions (wavelength, nm) and the intensities (oscillator strength) are also given in the Supporting Information. The first twelve transitions for the three compounds have been calculated. In the case of salt **11c**, only the first transition at 410 nm is intense, whereas the other transitions are smaller. The first transition at 410 nm is caused by an allowed excitation from the HOMO to the LUMO. Its value is close to the measured spectra in acetonitrile (408 nm). Calculations of the salt **11d** give two transitions at 446 and 351 nm. The first mentioned transition corresponds

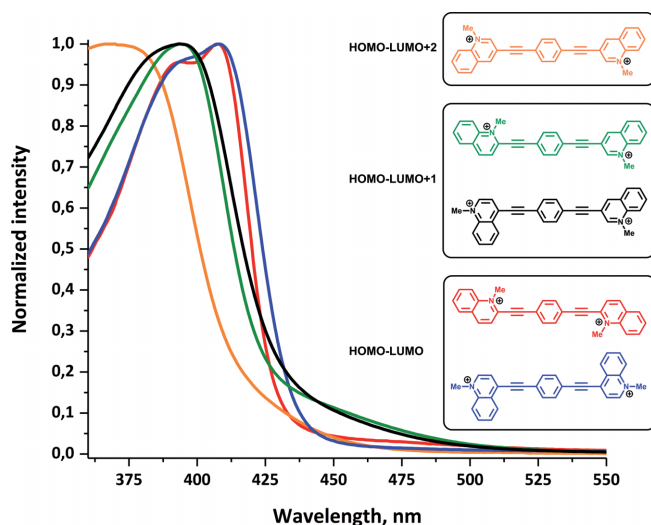


Figure 2. UV/Vis spectra of **11a–e** in acetonitrile, respectively.

to the HOMO-LUMO excitation, and the second, which is more intense, is the HOMO-LUMO+2 excitation. All frontier orbitals are given in Supporting Information. The measured UV/Vis spectra of **11d** display absorptions in the range from 367 to 371 nm which likely correspond to the HOMO-LUMO+2 excitation. In the case of the salt **11a**, calculations do not show only one, but several allowed transitions. The first one at 420 nm corresponds to the HOMO-LUMO excitation, whereas the second one at 392 nm is the HOMO-LUMO+1 transition. In addition, some weaker absorptions have been calculated at 322, 315, and 292 nm, respectively. Considering that the calculated UV spectra were performed in vacuo the spectra show the correct tendency with the experimental data.

Conclusions

The phenomena of conjugation and cross-conjugation are well reflected in the properties of dicationic salts which were prepared as model compounds for conjugation/conjugation, cross-conjugation/cross-conjugation as well as conjugation/cross-conjugation combinations. The types of conjugation can well be differentiated by means of ^{13}C NMR, IR, Raman, and UV/Vis spectroscopy.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen in flame or oven-dried glassware. All chemicals were purchased and used without further purification unless otherwise mentioned. Anhydrous solvents were dried according to standard procedures before usage. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). The ATR-IR spectra were obtained on a Bruker Alpha in the range of 400 to 4000 cm^{-1} . ^1H NMR spectra were recorded at 400 MHz or 600 MHz. ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz, with the solvent peak used as the internal reference. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Signal orientations in DEPT experiments were described as follows: o = no signal; + = up (CH,

CH_3); - = down (CH_2). The electrospray ionization mass spectra (ESI-MS) were measured with a Bruker Impact-II mass spectrometer. Samples were sprayed from MeCN. Chromatography: The reactions were traced by thin layer chromatography with silica gel 60 (F_{254} , MERCK KGAA). For the detection of substances, quenching was used at either 254 nm or 366 nm with a mercury lamp. The preparative column chromatography was conducted through silica gel 60 (230–400 mesh).

Calculations: All density-functional theory (DFT)-calculations were carried out by using the Firefly 8.2.0 QC package,^[21] which is partially based on the GAMESS (US)^[22] source code, running on Linux 2.6.18–238.el5 SMP (x86_64) on five AMD Phenom II X6 1090T processor workstations (Beowulf-cluster) with Infiniband interconnect and parallelized with MPICH 1.2.7p1. MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented 6-31G* basis set and with the PBE0 density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies. UV/Vis transitions were obtained by time-dependent (TD)-DFT calculations on the same level of theory. Orbital plots were obtained using J mol 14.27.2. Partial charges were obtained with NBO 5.9^[23] from the results of the DFT calculations.

General Procedure of the Sonogashira-Hagihara Coupling (Procedure 1): The reactions were carried out under a nitrogen atmosphere. A mixture of 5 mmol of the aryl halides, 1 mol-% of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 2 mol-% of CuI was suspended in 7 mL of anhydrous NEt_3 with stirring. A sample of the corresponding ethyne (1.05 equiv.) in dry NEt_3 was added dropwise at ambient temperature. The resulting solutions were then stirred at reflux temperature until complete conversion was monitored by TLC. The mixtures were then cooled to r.t.. The solvents were removed in vacuo. The resulting residues were finally purified by column chromatography (petroleum ether/ethyl acetate) to afford the products.

4,4'-Benzene-1,4-diylbis(2-methylbut-3-yn-2-ol) (7): According to Procedure 1, a solution of 4.720 g (20.00 mmol) of 1,4-dibromobenzene **6**, 0.140 g (0.2 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 0.076 g (0.4 mmol) of CuI, and 5.040 g (60.00 mmol) of MEBYNOL in 50 mL of anhydrous NEt_3 were reacted. Yield 4.792 g, 99 %, a white solid, m.p. 159–160 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.35 (m, 4H, 2-H, 3-H, 5-H, 6-H), 2.04 (s, 2H, OH), 1.60 (s, 12H, CH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 131.9 (+, C2, C3, C5, C6), 122.5 (o, C1, C4), 95.5 (CCOH), 81.6 (CCCOH), 65.4 (COH), 31.4 (+, CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3332, 2980, 2931, 1507, 1460, 1441, 1396, 1361, 1272, 1187, 1141, 959, 904, 846, 835, 789, 588, 562, 469 cm^{-1} . Spectroscopic data are in agreement with those reported in the literature.^[24]

General Procedure of Synthesis of the Terminal Alkynes (Procedure 2): The reactions were carried out under a nitrogen atmosphere. A flask was charged with the protected acetylenes (1.00 mmol), KOH (1.05 mmol), K_3PO_4 (1.05 mmol), and anhydrous toluene (40 mL). Then the flask was immersed into a preheated oil bath (200 °C). The suspensions were stirred vigorously under reflux temperature until complete conversion, as monitored by TLC. The mixtures were then cooled to r.t. and filtered through a plug of celite, which was washed several times with toluene. After evaporation of the organic phase to dryness, the resulting residues were finally purified by column chromatography (petroleum ether/ethyl acetate) to afford the products.

1,4-Diethynylbenzene (8): According to Procedure 2, a solution of 3.630 g (15.00 mmol) of 4,4'-benzene-1,4-diylbis(2-methylbut-3-yn-2-ol) **7**, 0.882 g (15.75 mmol) of KOH and 3.339 g (15.75 mmol) of K_3PO_4 in 50 mL of anhydrous toluene was heated (0.25 h) under

reflux temperature. Finally, a purification by column chromatography (petroleum ether/ethyl acetate = 3:1) gave 1,4-diethynylbenzene **8**. Yield 1.603 g, 62 %, a white solid m.p. 93–94 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.44 (s, 4H, 2-H, 3-H, 5-H, 6-H), 3.17 (s, 2H, CCH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 132.0 (+, C2, C3, C5, C6), 122.5 (o, C1, C4), 83.0 (o, CCH), 79.1 (o, CCH) ppm. IR (ATR): $\tilde{\nu}$ = 3260, 2104, 1919, 1668, 1506, 1495, 1404, 1368, 1251, 1170, 1105, 1016, 964, 905, 833, 675, 620, 545, 492 cm^{-1} . Spectroscopic data are in agreement with those reported in the literature.^[25]

3-((4-Ethynylphenyl)ethynyl)quinoline (9): According to Procedure 1, a solution of 2.080 g (10.00 mmol) of 3-bromoquinoline, 0.070 g (0.10 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 0.038 g (0.20 mmol) of CuI , and 1.197 g (9.50 mmol) of 1,4-diethynylbenzene **8** in 50 mL of anhydrous NEt_3 was heated (3.5 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether/ethyl acetate = 3:1) gave compound **9**. Yield 0.889 g, 37 %, a brown solid, m.p. 113–114 °C. ^1H NMR (600 MHz, CDCl_3): δ = 8.99 (d, J = 2.1 Hz, 1H, 2-H), 8.30 (d, J = 2.1 Hz, 1H, 4-H), 8.10 (d, J = 8.5 Hz, 1H, 8-H), 7.70 (d, J = 8.1 Hz, 1H, 5-H), 7.73 (ddd, J = 1.5, 7.0, 8.5 Hz, 1H, 7-H), 7.57 (ddd, J = 1.5, 7.0, 8.1 Hz, 1H, 6-H), 7.55–7.53 (m, 2H, 2'-H, 6'-H), 7.51–7.49 (m, 2H, 3'-H, 5'-H), 3.20 (s, 1H, CCH) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 152.1 (+, C2), 147.1 (o, C8a), 138.5 (+, C4), 132.3 (+, C3', C5'), 131.7 (+, C2', C6'), 130.4 (+, C7), 129.6 (+, C8), 127.8 (+, C5), 127.5 (+, C6), 127.4 (o, C4a), 123.2 (o, C1'), 122.6 (o, C4'), 117.2 (o, C3), 92.1 (o, C β), 88.7 (o, C α), 83.2 (o, C γ), 79.4 (o, C δ) ppm. IR (ATR): $\tilde{\nu}$ = 3265, 3060, 3034, 2101, 1969, 1710, 1699, 1602, 1566, 1487, 1404, 1351, 1266, 1145, 1105, 1010, 981, 958, 906, 861, 838, 782, 752, 691, 653, 622, 548, 471, 419 cm^{-1} . HRMS (ESI): m/z calcd. for $\text{C}_{19}\text{H}_{12}\text{N}$ [$\text{M}+\text{H}$] $^+$ 254.0964, found 254.0972; m/z calcd. for $\text{C}_{19}\text{H}_{11}\text{NNa}$ [$\text{M}+\text{Na}$] $^+$ 276.0789, found 276.0785.

2-((4-(Quinolin-3-ylethynyl)phenyl)ethynyl)quinoline (10a): According to Procedure 1, a solution of 0.017 g (0.11 mmol) of 2-chloroquinoline, 0.007 g (0.01 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 0.0038 g (0.02 mmol) of CuI , and 0.030 g (0.12 mmol) of 3-((4-ethynylphenyl)ethynyl)quinoline in 10 mL of anhydrous NEt_3 was heated for 3.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether/ethyl acetate = 3:1) gave compound **10a**. Yield 0.035 g, 80 %, a yellow solid, m.p. 197–198 °C. ^1H NMR (600 MHz, CDCl_3): δ = 9.01 (s, 1H, 2-H), 8.32 (d, J = 1.9 Hz, 1H, 4-H), 8.16–8.13 (m, 2H, 4'-H, 8'-H), 7.81–7.80 (m, 2H, 5-H, 5'-H), 7.76–7.72 (m, 2H, 7-H, 7'-H), 7.68–7.67 (m, 2H, 3'-H, 5''-H), 7.61 (d, J = 8.5 Hz, 1H, 3'-H), 7.60–7.59 (m, 2H, 2''-H, 6''-H), 7.58–7.54 (m, 2H, 6-H, 6'-H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 152.1 (+, C2), 148.4 (o, C8a'), 147.0 (o, C8a), 143.4 (o, C2'), 138.6 (+, C4), 136.4 (+, C4'), 132.4 (+, C3'', C5''), 131.9 (+, C2'', C6''), 130.4 (+, C7), 130.3 (+, C7'), 129.54 (+, C8), 129.49 (+, C8'), 127.8 (+, C5), 127.7 (+, C5'), 127.5 (+, C6), 127.41 (+, C6'), 127.37 (o, C4a), 127.3 (o, C4a'), 124.5 (+, C3'), 123.5 (o, C1''), 122.6 (o, C4''), 117.3 (o, C3), 92.3 (o, C β), 91.4 (o, C δ), 89.4 (o, C γ), 89.0 (o, C α) ppm. IR (ATR): $\tilde{\nu}$ = 3051, 3037, 2958, 2922, 2851, 2210, 1738, 1733, 1615, 1593, 1550, 1488, 1460, 1405, 1352, 1342, 1306, 1288, 1242, 1158, 1115, 1106, 1046, 1012, 980, 955, 912, 871, 850, 828, 790, 748, 693, 626, 613, 552, 520, 472, 429 cm^{-1} . HRMS (ESI): m/z calcd. for $\text{C}_{28}\text{H}_{16}\text{N}_2$ [$\text{M}+\text{H}$] $^+$ 381.1386, found 381.1382.

3-((4-(Quinolin-4-ylethynyl)phenyl)ethynyl)quinoline (10b): According to Procedure 1, a solution of 0.208 g (1.00 mmol) of 4-bromoquinoline, 0.070 g (0.10 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 0.038 g (0.20 mmol) of CuI , and 0.278 g (1.10 mmol) of 3-((4-ethynylphenyl)ethynyl)quinoline in 25 mL of anhydrous NEt_3 was heated for 3.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether/ethyl acetate = 3:1) gave compound **10b**. Yield 0.228 g, 61 %, a yellow solid, m.p. 153–154 °C. ^1H

NMR (600 MHz, CDCl_3): δ = 9.02 (d, J = 2.1 Hz, 1H, 2-H), 8.92 (d, J = 4.3 Hz, 1H, 2'-H), 8.37 (d, J = 8.3 Hz, 1H, 5'-H), 8.33 (s, 1H, 4-H), 8.16 (d, J = 8.1 Hz, 1H, 8'-H), 8.12 (d, J = 8.5 Hz, 1H, 8-H), 7.81 (d, J = 7.9 Hz, 1H, 5-H), 7.80–7.77 (m, 1H, 7'-H), 7.76–7.73 (m, 1H, 7-H), 7.68 (d, J = 8.3 Hz, 2H, 3''-H, 5''-H), 7.67–7.65 (m, 1H, 6'-H), 7.64 (d, J = 8.3 Hz, 2H, 2''-H, 6''-H), 7.60–7.57 (m, 2H, 6-H, 3'-H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 152.1 (+, C2), 149.7 (+, C2'), 148.0 (o, C8a'), 147.1 (o, C8a), 138.6 (+, C4), 132.2 (+, C3'', C5''), 132.0 (+, C2'', C6''), 130.5 (+, C7), 130.3 (+, C7'), 129.9 (+, C8'), 129.7 (o, C4'), 129.6 (+, C8), 127.81 (+, C5), 127.76 (o, C4a'), 127.57 (+, C6), 127.54 (+, C6'), 127.36 (o, C4a), 126.1 (+, C5), 123.78 (o, C1''), 123.75 (+, C3'), 122.6 (o, C4''), 117.2 (o, C3), 98.4 (o, C γ), 92.2 (o, C β), 89.3 (o, C α), 87.2 (o, C δ) ppm. IR (ATR): $\tilde{\nu}$ = 3033, 2210, 2188, 1733, 1575, 1511, 1486, 1462, 1418, 1393, 1351, 1294, 1194, 1101, 1012, 981, 954, 906, 864, 829, 782, 746, 678, 641, 592, 543, 476, 463, 419 cm^{-1} . HRMS (ESI): m/z calcd. for $\text{C}_{28}\text{H}_{16}\text{N}_2$ [$\text{M}+\text{H}$] $^+$ 381.1386, found 381.1384.

2,2'-(Benzene-1,4-diyl)diethyne-2,1-diyl)diquinoline (10c): According to Procedure 1, a solution of 0.408 g (2.50 mmol) of 2-chloroquinoline, 0.070 g (0.10 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 0.038 g (0.20 mmol) of CuI and 0.126 g (1.00 mmol) of 1,4-diethynylbenzene in 10 mL of anhydrous NEt_3 was heated (3.5 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether/ethyl acetate = 3:1) gave compound **10c**. Yield 0.209 g, 55 %, a yellow solid, m.p. 207–208 °C. ^1H NMR (600 MHz, CDCl_3): δ = 8.17 (d, J = 8.1 Hz, 2H, 4-H, 4'-H), 8.13 (d, J = 7.9 Hz, 2H, 8-H, 8'-H), 7.80 (d, J = 8.1 Hz, 2H, 5-H, 5'-H), 7.74 (ddd, J = 1.4, 6.8, 7.9 Hz, 2H, 7-H, 7'-H), 7.66 (s, 4H, 2''-H, 3''-H, 5''-H, 6''-H), 7.60 (d, J = 8.1 Hz, 3-H, 3'-H), 7.55 (ddd, J = 1.4, 6.8, 8.1 Hz, 2H, 6-H, 6'-H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 148.3 (o, C8a, C8a'), 143.3 (o, C2, C2'), 136.3 (+, C4, C4'), 132.2 (+, C2'', C3'', C5'', C6''), 130.2 (+, C7, C7'), 129.4 (+, C8, C8'), 127.6 (+, C5, C5'), 127.3 (+, C6, C6'), 127.2 (o, C4a, C4a'), 124.4 (+, C3, C3'), 122.9 (o, C1'', C4''), 91.4 (o, C α , C δ), 89.3 (o, C β , C γ) ppm. IR (ATR): $\tilde{\nu}$ = 3056, 2211, 2186, 1590, 1548, 1505, 1419, 1289, 1107, 971, 950, 830, 790, 748, 629, 555, 480 cm^{-1} . HRMS (ESI): m/z calcd. for $\text{C}_{28}\text{H}_{16}\text{N}_2$ [$\text{M}+\text{H}$] $^+$ 381.1386, found 381.1390.

3,3'-(Benzene-1,4-diyl)diethyne-2,1-diyl)diquinoline (10d): According to Procedure 1, a solution of 0.520 g (2.50 mmol) of 3-bromoquinoline, 0.070 g (0.10 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 0.038 g (0.20 mmol) CuI , and 0.126 g (1.00 mmol) of 1,4-diethynylbenzene in 10 mL of anhydrous NEt_3 was heated for 3.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether/ethyl acetate = 3:1) gave 3,3'-compound **10d**. Yield 0.095 g, 25 %, a yellow solid, m.p. 203–204 °C. ^1H NMR (600 MHz, CDCl_3): δ = 9.00 (d, J = 2.0 Hz, 2H, 2-H, 2'-H), 8.32 (d, J = 2.0 Hz, 2H, 4-H, 4'-H), 8.11 (d, J = 8.1 Hz, 2H, 8-H, 8'-H), 7.81 (d, J = 7.7 Hz, 2H, 5-H, 5'-H), 7.73 (ddd, J = 1.5, 7.0, 8.1 Hz, 2H, 7-H, 7'-H), 7.60 (s, 4H, 2''-H, 3''-H, 5''-H, 6''-H), 7.58 (ddd, J = 1.5, 7.0, 7.7 Hz, 2H, 6-H, 6'-H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 152.1 (+, C2, C2'), 147.1 (o, C8a, C8a'), 138.5 (+, C4, C4'), 131.9 (+, C2'', C3'', C5'', C6''), 130.4 (+, C7, C7'), 129.6 (+, C8, C8'), 127.8 (+, C5, C5'), 127.5 (+, C6, C6'), 127.4 (o, C4a, C4a'), 123.1 (o, C1'', C4''), 117.3 (o, C3, C3'), 92.3 (o, C β , C γ), 88.9 (o, C α , C δ) ppm. IR (ATR): $\tilde{\nu}$ = 3066, 3055, 3016, 1838, 1567, 1486, 1354, 1101, 981, 958, 906, 863, 830, 785, 746, 641, 620, 569, 547, 516, 474, 459, 432 cm^{-1} . HRMS (ESI): m/z calcd. for $\text{C}_{28}\text{H}_{16}\text{N}_2$ [$\text{M}+\text{H}$] $^+$ 381.1386, found 381.1387.

4,4'-(Benzene-1,4-diyl)diethyne-2,1-diyl)diquinoline (10e): According to Procedure 1, a solution of 0.520 g (2.50 mmol) of 4-bromoquinoline, 0.070 g (0.10 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 0.038 g (0.20 mmol) CuI , and 0.126 g (1.00 mmol) of 1,4-diethynylbenzene in 10 mL of anhydrous NEt_3 was heated (3.5 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether/ethyl acetate = 3:1) gave compound **10e**. Yield 0.103 g, 27 %, ^1H

an orange solid, m.p. 225–226 °C (decomp.). ¹H NMR (600 MHz, CDCl₃): δ = 8.93 (d, *J* = 4.4 Hz, 2H, 2-H, 2'-H), 8.37 (ddd, *J* = 0.5, 1.4, 8.3 Hz, 2H, 5-H, 5'-H), 8.15 (ddd, *J* = 0.5, 1.3, 8.5 Hz, 2H, 8-H, 8'-H), 7.79 (dd, *J* = 1.3, 6.9, 8.4 Hz, 2H, 7-H, 7'-H), 7.72 (s, 4H, 2''-H, 3''-H, 5''-H, 6''-H), 7.67 (ddd, *J* = 1.3, 6.9, 8.4 Hz, 2H, 6-H, 6'-H), 7.59 (d, *J* = 4.4 Hz, 2H, 3-H, 3'-H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 149.9 (+, C2, C2'), 148.3 (o, C8a, C8a'), 132.2 (+, C2'', C3'', C5'', C6''), 130.2 (+, C8, C8'), 130.1 (+, C7, C7'), 129.4 (o, C4, C4'), 127.7 (o, C4a, C4a'), 127.5 (+, C6, C6'), 126.0 (+, C5, C5'), 123.8 (+, C3, C3'), 123.3 (o, C1'', C4''), 98.0 (o, Cβ, Cγ), 87.5 (o, Cα, Cδ) ppm. IR (ATR): ν̄ = 2981, 1733, 1576, 1561, 1506, 1495, 1461, 1435, 1389, 1361, 1272, 1154, 1134, 1102, 1027, 961, 904, 868, 846, 759, 722, 691, 642, 625, 571, 547, 470, 442 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₂₈H₁₆N₂ [M+H]⁺ 381.1386, found 381.1390.

General Procedure for the Preparation of the salts 11a–e (Procedure 3): Samples of 0.50 mmol of the corresponding quinolines **10a–e** were dissolved in toluene containing 1 drop of nitrobenzene. Then an excess of dimethyl sulfate was added with stirring. Thereafter the resulting mixture was stirred under reflux temperature. After completion of the reaction (controlled by TLC), the solution was cooled, the crude product was filtered off, washed with ethyl acetate (3 × 10 mL), and dried to afford the products.

1-Methyl-2-((4-((1-methylquinolinium-3-yl)ethynyl)phenyl)ethynyl)quinolinium dimethylsulfate (11a): According to Procedure 3, a solution of 0.048 g (0.125 mmol) of 2-((4-(quinolin-3-ylethynyl)phenyl)ethynyl)quinoline **10a**, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated over the period of 3 h under reflux temperature to give compound **11a**. Yield 0.078 g, 99 %, a yellow solid, m.p. 205–206 °C (decomp.). ¹H NMR (600 MHz, [D₆]DMSO): δ = 9.91 (d, *J* = 0.9 Hz, 1H, 2-H), 9.55 (s, 1H, 4-H), 9.26 (d, *J* = 8.6 Hz, 1H, 4'-H), 8.62 (d, *J* = 8.9 Hz, 1H, 8'-H), 8.56 (d, *J* = 9.0 Hz, 1H, 8-H), 8.48–8.46 (m, 3H, 5-H, 3'-H, 5'-H), 8.36–8.31 (m, 2H, 7-H, 7'-H), 8.14–8.11 (m, 3H, 6-H, 3''-H, 5''-H), 8.07 (t, *J* = 7.6 Hz, 1H, 6'-H), 7.91 (d, *J* = 8.4 Hz, 2H, 2''-H, 6''-H), 4.80 (s, 3H, N'CH₃), 4.67 (s, 3H, NCH₃), 3.37 (s, 6H, 2 CH₃SO₄) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): δ = 152.2 (+, C2), 148.3 (+, C4), 145.6 (+, C4'), 140.2 (o, C2'), 139.4 (o, C8a'), 137.5 (o, C8a), 136.4 (+, C7), 136.2 (+, C7'), 133.6 (+, C3'', C5''), 132.4 (+, C2'', C6''), 130.7 (+, C6), 130.44 (+, C5 or C5'), 130.37 (+, C5 or C5'), 130.2 (+, C6'), 128.7 (o, C4a), 128.6 (o, C4a'), 126.3 (+, C3'), 124.1 (o, C1'), 120.1 (o, C4'), 119.6 (+, C8'), 119.3 (+, C8), 116.2 (o, C3), 107.1 (o, Cγ), 93.6 (o, Cβ), 86.8 (o, Cα), 84.6 (o, Cδ), 52.8 (+, 2 CH₃SO₄), 45.5 (+, NCH₃), 42.9 (+, N'CH₃) ppm. IR (ATR): ν̄ = 3049, 2200, 1594, 1575, 1520, 1455, 1437, 1408, 1377, 1354, 1307, 1216, 1155, 1056, 1001, 838, 735, 609, 577, 552, 497, 429 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₃₀H₂₂N₂ [M]²⁺ 205.0884, found 205.0886.

1-Methyl-3-((4-((1-methylquinolinium-4-yl)ethynyl)phenyl)ethynyl)quinolinium Dimethylsulfate (11b): According to Procedure 3, a solution of 0.048 g (0.125 mmol) of 3-((4-(quinolin-4-ylethynyl)phenyl)ethynyl)quinoline **10b**, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated over the period of 3 h under reflux temperature to give compound **11b**. Yield 0.078 g, 99 %, a yellow solid, m.p. 259–260 °C (decomp.). ¹H NMR (600 MHz, [D₆]DMSO): δ = 9.91 (d, *J* = 1.0 Hz, 1H, 2-H), 9.55 (s, 1H, 4-H), 9.53 (d, *J* = 6.4 Hz, 1H, 2'-H), 8.81 (d, *J* = 9.0 Hz, 1H, 5'-H), 8.58 (d, *J* = 9.0 Hz, 1H, 8'-H), 8.56 (d, *J* = 9.0 Hz, 1H, 8-H), 8.47 (d, *J* = 7.8 Hz, 1H, 5-H), 8.37–8.32 (m, 2H, 7-H, 7'-H), 8.17 (t, *J* = 7.5 Hz, 1H, 6'-H), 8.12 (t, *J* = 7.5 Hz, 1H, 6-H), 8.09 (d, *J* = 8.3 Hz, 2H, 3''-H, 5''-H), 7.89 (d, *J* = 8.3 Hz, 2H, 2''-H, 6''-H), 4.67 (s, 3H, NCH₃), 4.64 (s, 3H, N'CH₃), 3.37 (s, 6H, 2 CH₃SO₄) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): δ = 152.2 (+, C2), 149.5 (+, C2'), 148.3 (+, C4), 138.4 (o, C8a'), 138.0 (o, C4'), 137.5 (o, C8a), 136.3 (+,

C7), 135.8 (+, C7'), 133.4 (+, C3'', C5''), 132.3 (+, C2'', C6''), 130.9 (+, C6'), 130.7 (+, C6), 130.4 (+, C5), 128.7 (o, C4a), 128.4 (o, C4a'), 127.9 (+, C5'), 124.4 (+, C3'), 123.3 (o, C1''), 121.3 (o, C4''), 119.9 (+, C8'), 119.3 (+, C8), 116.3 (o, C3), 105.8 (o, Cγ), 93.8 (o, Cβ), 86.4 (o, Cα), 86.2 (o, Cδ), 52.8 (+, 2 CH₃SO₄), 45.5 (+, NCH₃), 45.4 (+, N'CH₃) ppm. IR (ATR): ν̄ = 3083, 3049, 2945, 2203, 2162, 1604, 1569, 1520, 1405, 1372, 1326, 1244, 1226, 1214, 1058, 1011, 904, 844, 771, 737, 609, 575, 552, 500, 486, 465, 430 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₃₀H₂₂N₂ [M]²⁺ 205.0884, found 205.0885.

2,2'-(Benzene-1,4-diyl)diethyne-2,1-diylbis(1-methylquinolinium) Dimethylsulfate (11c): According to Procedure 3, a solution of 0.048 g (0.125 mmol) of 2,2'-(benzene-1,4-diyl)diethyne-2,1-diyl)diquinoline **10c**, 1 drop of nitrobenzene, and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 3 h under reflux temperature to give **11c**. Yield 0.079 g, 99 %, a yellow solid m.p. 241–242 °C (decomp.). ¹H NMR (600 MHz, [D₆]DMSO): δ = 9.28 (d, *J* = 8.6 Hz, 2H, 4-H, 4'-H), 8.63 (d, *J* = 8.8 Hz, 2H, 8-H, 8'-H), 8.49 (d, *J* = 8.3 Hz, 2H, 3-H, 3'-H), 8.48 (d, *J* = 7.5 Hz, 2H, 5-H, 5'-H), 8.33 (t, *J* = 7.7 Hz, 2H, 7-H, 7'-H), 8.19 (s, 4H, 2''-H, 3''-H, 5''-H, 6''-H), 8.07 (t, *J* = 7.5 Hz, 2H, 6-H, 6'-H), 4.81 (s, 6H, NCH₃), 3.37 (s, 6H, 2 CH₃SO₄) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): δ = 145.7 (+, C4, C4'), 140.3 (o, C2, C2'), 139.4 (o, C8a, C8a'), 136.2 (+, C7, C7'), 133.6 (+, C2'', C3'', C5'', C6''), 130.4 (+, C5, C5'), 130.2 (+, C6, C6'), 128.7 (o, C4a, C4a'), 126.4 (+, C3, C3'), 122.1 (o, C1'', C4''), 119.6 (+, C8, C8'), 106.6 (o, Cβ, Cγ), 85.1 (o, Cα, Cδ), 52.8 (+, 2 CH₃SO₄), 43.0 (+, NCH₃, N'CH₃) ppm. IR (ATR): ν̄ = 3070, 2203, 1615, 1594, 1575, 1521, 1437, 1353, 1160, 1045, 1000, 838, 744, 576, 553, 498, 476, 428 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₃₀H₂₂N₂ [M]²⁺ 205.0884, found 205.0889.

3,3'-(Benzene-1,4-diyl)diethyne-2,1-diylbis(1-methylquinolinium) Dimethylsulfate (11d): According to Procedure 3, a solution of 0.048 g (0.125 mmol) of 3,3'-(benzene-1,4-diyl)diethyne-2,1-diyl)diquinoline **10d**, 1 drop of nitrobenzene, and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 3 h under reflux temperature to give **11d**. Yield 0.078 g, 99 %, a yellow solid, m.p. 265 °C (decomp.). ¹H NMR (600 MHz, [D₆]DMSO): δ = 9.89 (d, *J* = 1.0 Hz, 2H, 2-H, 2'-H), 9.53 (s, 2H, 4-H, 4'-H), 8.55 (d, *J* = 8.9 Hz, 2H, 8-H, 8'-H), 8.47 (d, *J* = 7.5 Hz, 2H, 5-H, 5'-H), 8.33 (ddd, *J* = 1.6, 7.1, 8.7 Hz, 2H, 7-H, 7'-H), 8.11 (t, *J* = 7.9 Hz, 2H, 6-H, 6'-H), 7.83 (s, 4H, 2''-H, 3''-H, 5''-H, 6''-H), 4.67 (s, 6H, 2NCH₃), 3.37 (s, 6H, 2 CH₃SO₄) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): δ = 152.2 (+, C2, C2'), 148.2 (+, C4, C4'), 137.4 (o, C8a, C8a'), 136.3 (+, C7, C7'), 132.3 (+, C2'', C3'', C5'', C6''), 130.7 (+, C6, C6'), 130.4 (+, C5, C5') 128.7 (o, C4a, C4a'), 122.1 (o, C1'', C4''), 119.3 (+, C8, C8'), 116.4 (o, C3, C3'), 93.9 (o, Cβ, Cγ), 85.8 (o, Cα, Cδ), 52.8 (+, 2 CH₃SO₄), 45.5 (+, NCH₃, N'CH₃) ppm. IR (ATR): ν̄ = 3045, 2219, 1629, 1605, 1580, 1520, 1448, 1378, 1358, 1214, 1168, 1140, 1057, 1002, 920, 846, 773, 733, 609, 576, 552, 432 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₃₀H₂₂N₂ [M]²⁺ 205.0884, found 205.0881.

4,4'-(Benzene-1,4-diyl)diethyne-2,1-diylbis(1-methylquinolinium) Dimethylsulfate (11e): According to Procedure 3, a solution of 0.048 g (0.125 mmol) of 4,4'-(benzene-1,4-diyl)diethyne-2,1-diyl)diquinoline **10e**, 1 drop of nitrobenzene, and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 3 h under reflux temperature to give **11e**. Yield 0.075 g, 93 %, a yellow solid, m.p. 218–219 °C (decomp.). ¹H NMR (600 MHz, [D₆]DMSO): δ = 9.52 (d, *J* = 6.0 Hz, 2H, 2-H, 2'-H), 8.80 (d, *J* = 8.3 Hz, 2H, 5-H, 5'-H), 8.57 (d, *J* = 8.8 Hz, 2H, 8-H, 8'-H), 8.40 (d, *J* = 6.0 Hz, 2H, 3-H, 3'-H), 8.35 (t, *J* = 7.8 Hz, 2H, 7-H, 7'-H), 8.16 (t, *J* = 7.5 Hz, 2H, 6-H, 6'-H), 8.12 (s, 4H, 2''-H, 3''-H, 5''-H, 6''-H), 4.64 (s, 6H, NCH₃, N'CH₃), 3.38 (s, 6H, 2 CH₃SO₄) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): δ = 149.5 (+, C2, C2'), 138.4 (o, C8a, C8a'), 137.8 (o, C4, C4'), 135.8

(+, C7, C7'), 133.4 (+, C2'', C3'', C5'', C6''), 130.9 (+, C6, C6'), 128.3 (+, C5, C5'), 127.9 (o, C4a, C4a'), 124.6 (+, C3, C3'), 122.5 (o, C1'', C4''), 119.8 (+, C8a, C8a'), 105.6 (o, C β , C γ), 86.6 (o, C α , C δ), 52.8 (+, 2 CH₃SO₄), 45.5 (+, NCH₃, N'CH₃) ppm. IR (ATR): $\tilde{\nu}$ = 3067, 3015, 2948, 2207, 1601, 1565, 1528, 1401, 1371, 1325, 1216, 1149, 1120, 1110, 1055, 994, 856, 807, 775, 738, 708, 646, 608, 577, 553, 488, 429 cm⁻¹. HRMS (ESI): m/z calcd. for C₃₀H₂₂N₂ [M]²⁺ 205.0884, found 205.0885.

General Procedure of Anion Exchange to Hexafluorophosphate (Procedure 4): The corresponding salt was dissolved in water, then NH₄PF₆ (1.05 equiv.) in water was added whereupon the hexafluorophosphate salt precipitated immediately. After 0.5 h the crude product was filtered off and washed with water (3 × 30 mL) and ethyl acetate (3 × 30 mL), and dried in vacuo. The assignment of atoms in ¹H/¹³C was performed according to compounds with methylsulfate anion (**11c–e**).

2,2'-(Benzene-1,4-diyl)diethyne-2,1-diylbis(1-methylquinolinium) Dihexafluorophosphate (11c2PF₆): According to Procedure 4, a solution of 0.045 g (0.071 mmol) of **11c** and 0.024 g (0.149 mmol) of NH₄PF₆ in 4 mL of water mixture was stirred over the period of 0.5 h at r.t. to give **11c2PF₆**. Yield 0.049 g, 98 %, a yellow solid, m.p. 226–227 °C. ¹H NMR (600 MHz, [D₆]DMSO): δ = 9.28 (d, J = 8.6 Hz, 2H, 4-H, 4'-H), 8.63 (d, J = 8.8 Hz, 2H, 8-H, 8'-H), 8.49 (d, J = 8.3 Hz, 2H, 3-H, 3'-H), 8.48 (d, J = 7.5 Hz, 2H, 5-H, 5'-H), 8.33 (t, J = 7.7 Hz, 2H, 7-H, 7'-H), 8.19 (s, 4H, 2''-H, 3''-H, 5''-H, 6''-H), 8.07 (t, J = 7.5 Hz, 2H, 6-H, 6'-H), 4.81 (s, 6H, 2NCH₃) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): δ = 145.7 (C4, C4'), 140.3 (C2, C2'), 139.4 (C8a, C8a'), 136.2 (C7, C7'), 133.6 (C2'', C3'', C5'', C6''), 130.4 (C5, C5'), 130.2 (C6, C6'), 128.7 (C4a, C4a'), 126.4 (C3, C3'), 122.1 (C1'', C4''), 119.6 (C8, C8'), 106.6 (C β , C γ), 85.1 (C α , C δ), 43.0 (NCH₃, N'CH₃) ppm. IR (ATR): $\tilde{\nu}$ = 3100, 2204, 2042, 1596, 1576, 1522, 1439, 1352, 1234, 1161, 1059, 819, 602, 555, 499, 471 cm⁻¹. HRMS (ESI): m/z calcd. for C₃₀H₂₂N₂ [M]²⁺ 205.0884, found 205.0881.

3,3'-(Benzene-1,4-diyl)diethyne-2,1-diylbis(1-methylquinolinium) Dihexafluorophosphate (11d2PF₆): According to Procedure 4, a solution of 0.020 g (0.031 mmol) of **11d** and 0.011 g (0.065 mmol) of NH₄PF₆ in 4 mL of water mixture was stirred over the period of 0.5 h at r.t. to give **11d2PF₆**. Yield 0.021 g, 99 %, a yellow solid, m.p. 224–225 °C. ¹H NMR (600 MHz, [D₆]DMSO): δ = 9.89 (d, J = 1.0 Hz, 2H, 2-H, 2'-H), 9.53 (s, 2H, 4-H, 4'-H), 8.55 (d, J = 8.9 Hz, 2H, 8-H, 8'-H), 8.47 (d, J = 7.5 Hz, 2H, 5-H, 5'-H), 8.33 (ddd, J = 1.6, 7.1, 8.7 Hz, 2H, 7-H, 7'-H), 8.11 (t, J = 7.9 Hz, 2H, 6-H, 6'-H), 7.83 (s, 4H, 2''-H, 3''-H, 5''-H, 6''-H), 4.67 (s, 6H, NCH₃, N'CH₃) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): δ = 152.2 (C2, C2'), 148.2 (C4, C4'), 137.4 (C8a, C8a'), 136.3 (C7, C7'), 132.3 (C2'', C3'', C5'', C6''), 130.7 (C6, C6'), 128.7 (C4a, C4a'), 122.1 (C1'', C4''), 119.3 (C8, C8'), 116.4 (C3, C3'), 93.9 (C β , C γ), 85.8 (C α , C δ), 45.5 (NCH₃, N'CH₃) ppm. IR (ATR): $\tilde{\nu}$ = 3095, 2230, 1607, 1581, 1521, 1435, 1378, 1359, 1318, 1222, 1117, 926, 823, 767, 622, 555, 494, 483, 433 cm⁻¹. HRMS (ESI): m/z calcd. for C₃₀H₂₂N₂ [M]²⁺ 205.0884, found 205.0882.

4,4'-(Benzene-1,4-diyl)diethyne-2,1-diylbis(1-methylquinolinium) Dihexafluorophosphate (11e2PF₆): According to Procedure 4, a solution of 0.020 g (0.031 mmol) of **11e** and 0.011 g (0.065 mmol) of NH₄PF₆ in 4 mL of water mixture was stirred over the period of 0.5 h at r.t. to give **11e2PF₆**. Yield 0.021 g, 99 %, a green solid, m.p. 341–342 °C (decomp.). ¹H NMR (600 MHz, [D₆]DMSO): δ = 9.52 (d, J = 6.0 Hz, 2H, 2-H, 2'-H), 8.80 (d, J = 8.3 Hz, 2H, 5-H, 5'-H), 8.57 (d, J = 8.8 Hz, 2H, 8-H, 8'-H), 8.40 (d, J = 6.0 Hz, 2H, 3-H, 3'-H), 8.35 (t, J = 7.8 Hz, 2H, 7-H, 7'-H), 8.16 (t, J = 7.5 Hz, 2H, 6-H, 6'-H), 8.12 (s, 4H, 2''-H, 3''-H, 5''-H, 6''-H), 4.64 (s, 6H, NCH₃, N'CH₃) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): δ = 149.5 (C2, C2'), 138.4 (C8a, C8a'), 137.8 (C4, C4'), 135.8 (C7, C7'), 133.4 (C2'', C3'',

C5'', C6''), 130.9 (C6, C6'), 128.3 (C5, C5'), 127.9 (C4a, C4a'), 124.6 (C3, C3'), 122.5 (C1'', C4''), 119.8 (C8a, C8a'), 105.6 (C β , C γ), 86.6 (C α , C δ), 45.5 (NCH₃, N'CH₃) ppm. IR (ATR): $\tilde{\nu}$ = 3327, 3102, 2209, 2167, 1619, 1604, 1574, 1530, 1508, 1436, 1403, 1373, 1335, 1326, 1237, 1204, 1179, 1155, 1116, 1105, 1019, 998, 828, 767, 712, 644, 556, 488, 437, 410 cm⁻¹. HRMS (ESI): m/z calcd. for C₃₀H₂₂N₂ [M]²⁺ 205.0884, found 205.0886.

Keywords: Betaines · Charge distribution · Mesomers · Polycations

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